

3rd NASA-NIST Workshop on Nanotube Measurements

September 26-28, 2007

Gaithersburg, MD, USA

Raman Spectroscopy and Nanotube Standards



UFMG

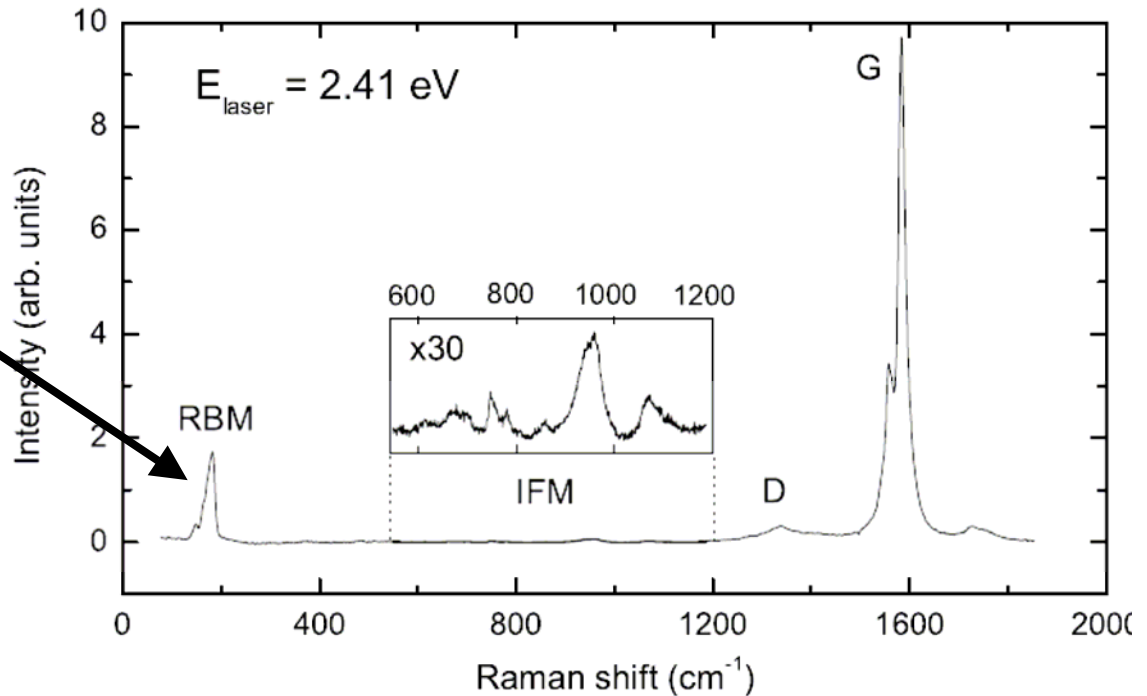
Ado Jorio



*Physics Department, UFMG, Belo Horizonte
and
Materials Division, INMETRO, Rio de Janeiro,
BRAZIL*

Outline

- The problem of Nano-Metrology (the MSIN07)
- The structural dependence of the RBM in single-wall carbon nanotubes



- The concept of nano-bulk consistency – establishing reference standards

**Attendance: 80 participants
(14 countries)**

Brazil – 43

USA – 9

Germany – 7

France – 5

Finland – 4

Mexico – 3

**Argentina, Canada, Czech Republic, Italy, Japan, Lithuania, UK
and the Netherlands – 1 each**

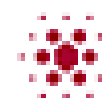
Universities and Research Institutes – 65

Metrology Institutes – 21 (mostly from Inmetro)

Industry – 4

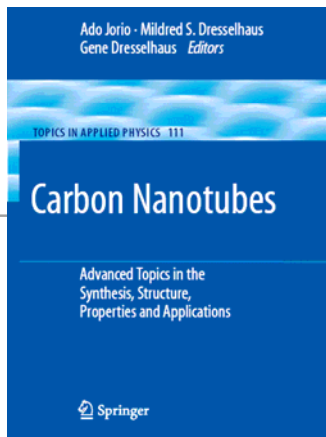


**INTERAMERICAN
SYSTEM OF
METROLOGIA**



FEI COMPANY™
TOOLS FOR NANOTECH

MSIN08 (Montpelier) is coming!!!

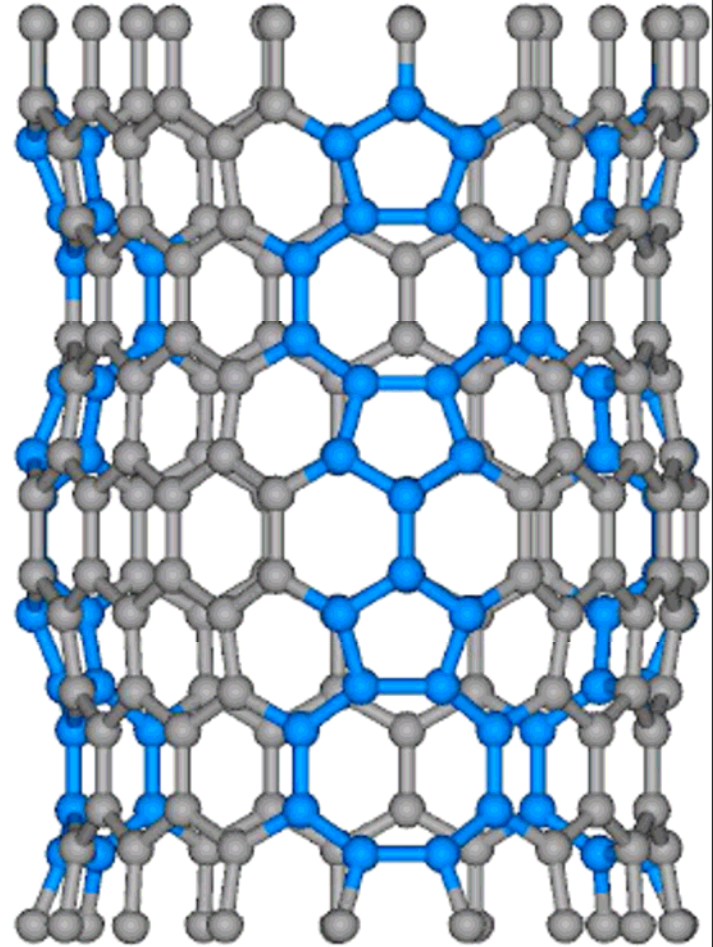
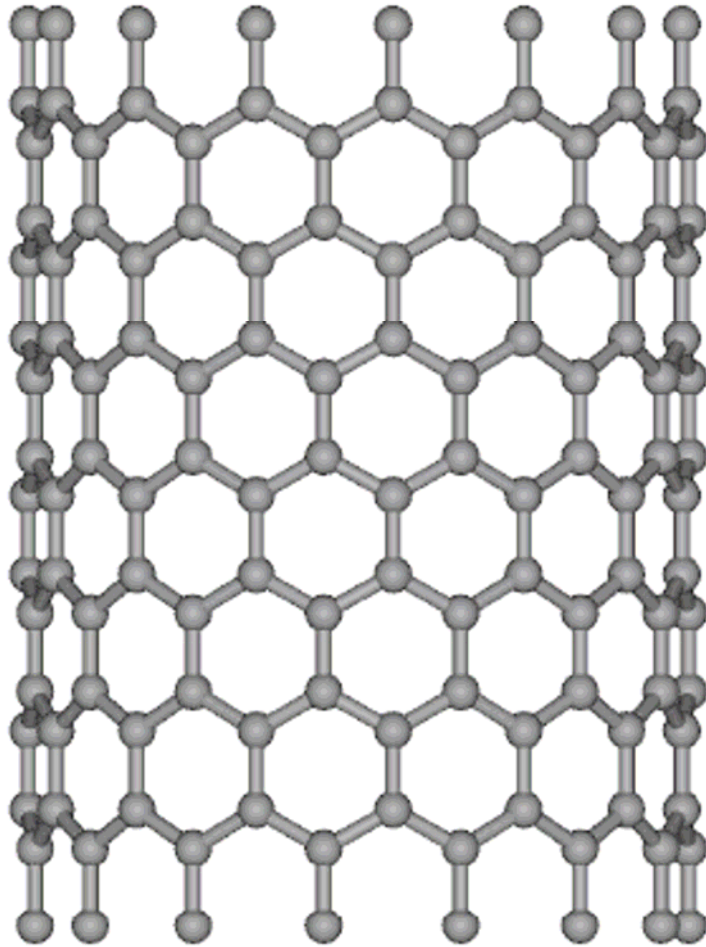


Applications of Carbon Nanotubes

by *M. Endo, M. S. Strano, P. M. Ajayan*

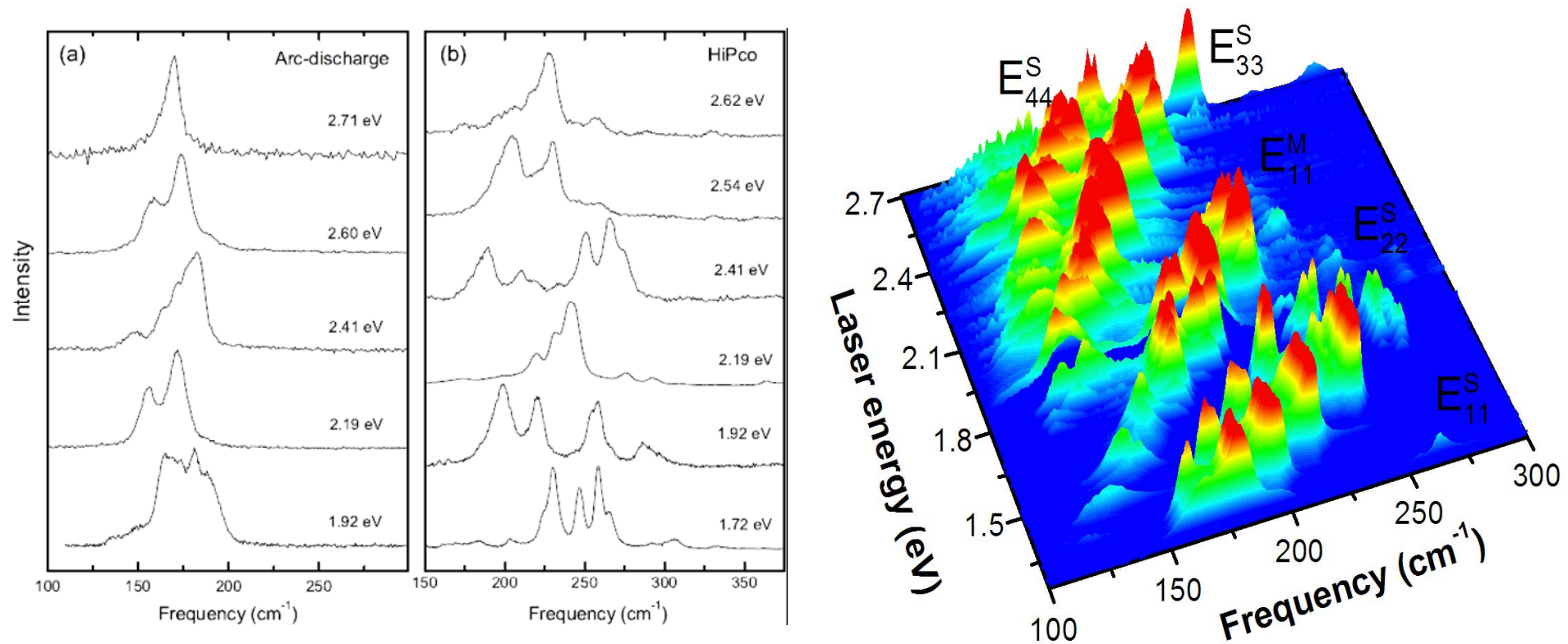
	Large Volume Applications	Limited Volume Applications (Mostly based on Engineered Nanotube Structures)
Present	<ul style="list-style-type: none"> - Battery Electrode Additives (MWNT) - Composites (sporting goods; MWNT) - Composites (ESD* applications; MWNT) *ESD – Electrical Shielding Device 	<ul style="list-style-type: none"> - Scanning Probe Tips (MWNT) - Specialized Medical Appliances (catheters) (MWNT)
Near Term (less than ten years)	<ul style="list-style-type: none"> - Battery and Super-capacitor Electrodes - Multifunctional Composites (3D, damping) - Fuel Cell Electrodes (catalyst support) - Transparent Conducting Films - Field Emission Displays / Lighting - CNT based Inks for Printing 	<ul style="list-style-type: none"> - Single Tip Electron Guns - Multi-Tip Array X-ray Sources - Probe Array Test Systems - CNT Brush Contacts - CNT Sensor Devices - Electro-mechanical Memory Device - Thermal Management Systems
Long Term (beyond ten years)	<ul style="list-style-type: none"> - Power Transmission Cables - Structural Composites (aerospace and automobile etc.) - CNT in Photovoltaic Devices 	<ul style="list-style-type: none"> - Nano-electronics (FET, Interconnects) - Flexible Electronics - CNT based bio-sensors - CNT Filtration/Separation Membranes - Drug-delivery Systems

What are the tube properties?



How are the tubes???

The RBM Resonance Raman Spectra (RRS)

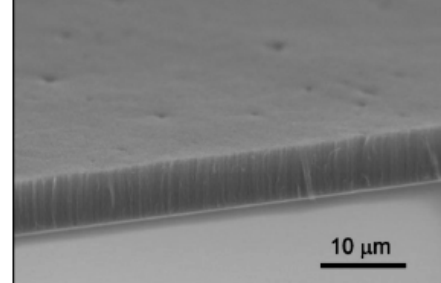


- depend on the diameter distribution in the sample: $\omega_{\text{RBM}} = A/d_t + B$
- depend on the excitation laser line (E_{laser}): resonance effect

The RBM resonance Raman map is a direct measure of the Kataura plot

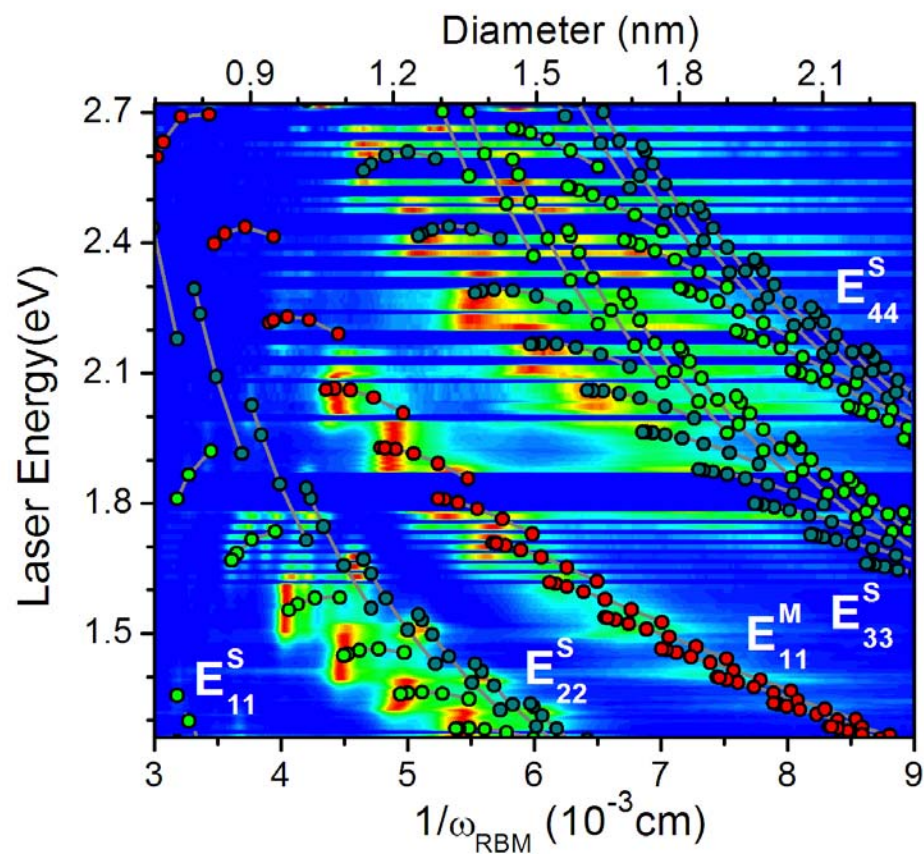
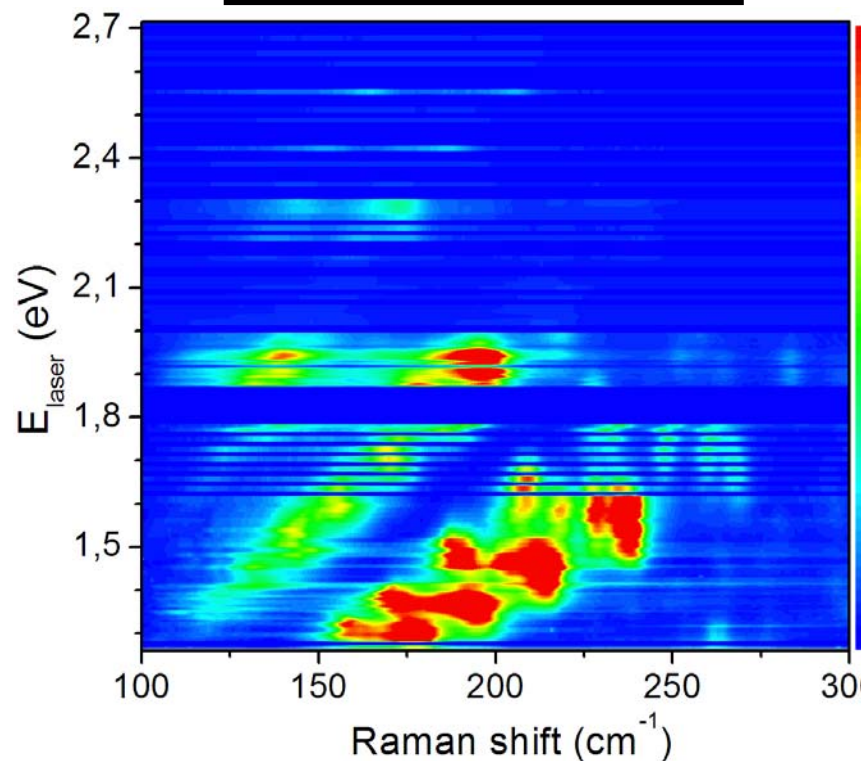
P. T. Araujo et al. PRL 98, 067401 (2007)

*Measurement ranges : energy - 1.26 to 2.71 eV
diameter - 0.7 to 2.3 nm*



*Sample:
SWNTs carpet – CVD
Y. Murakami et al.
Carbon 43, 2664 (2005)*

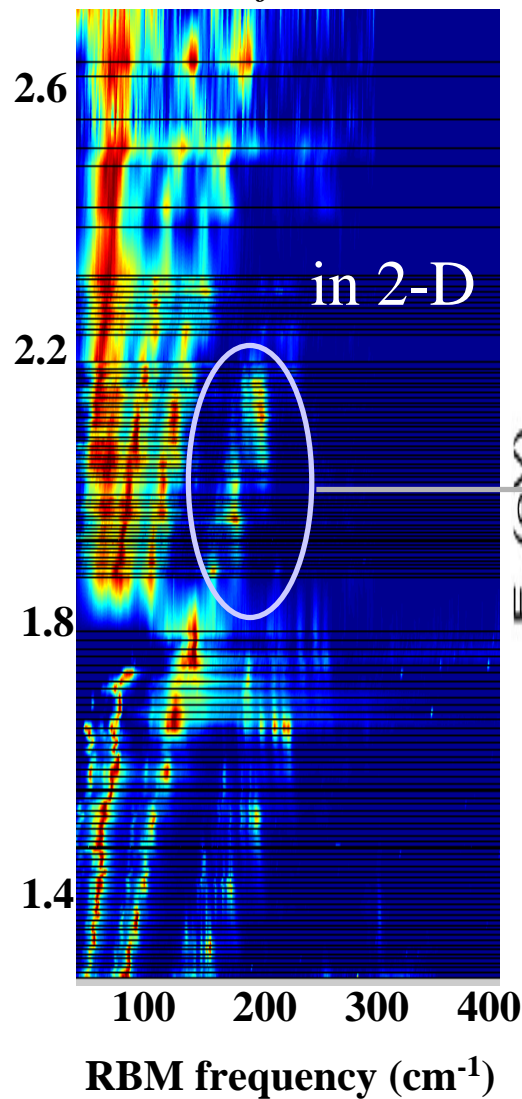
Real Intensity data



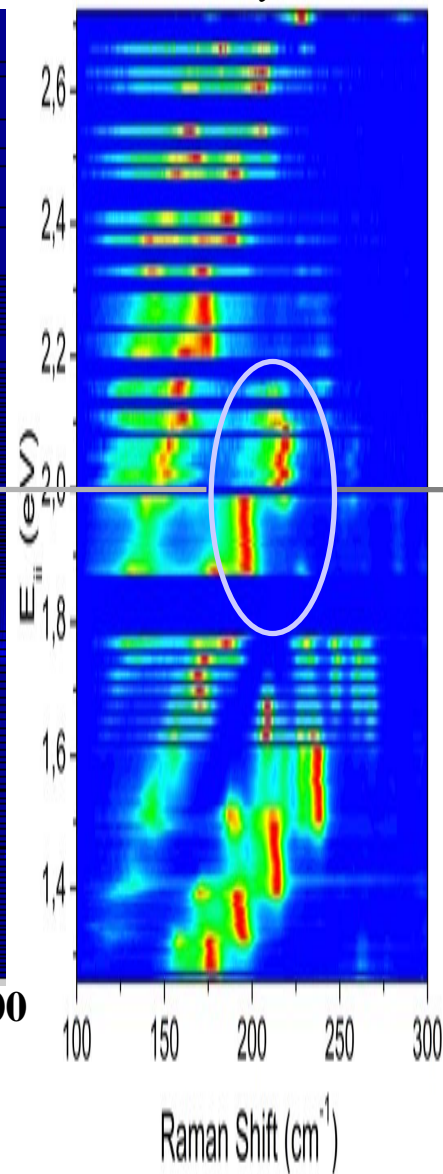
RRS to characterize synthesis and processing

Laser energy (eV)

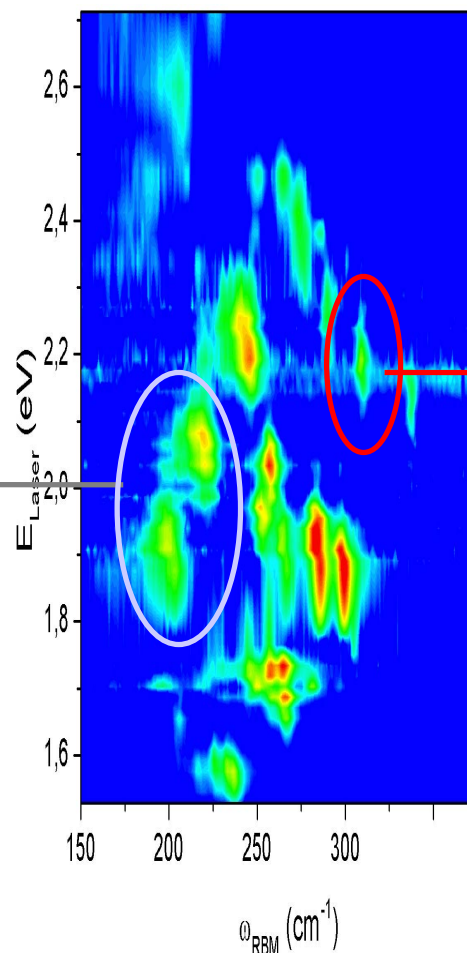
CVD water
Kenji Hata



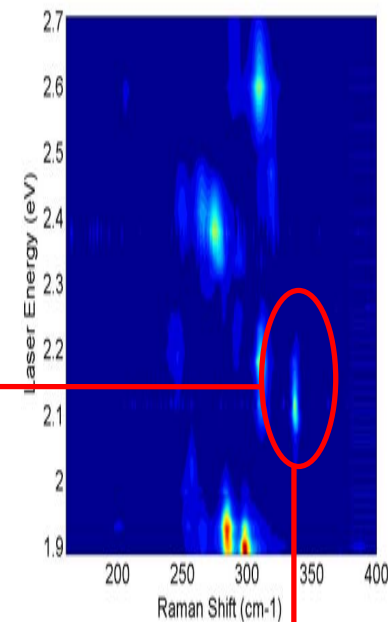
CVD alcohol
Maruyana



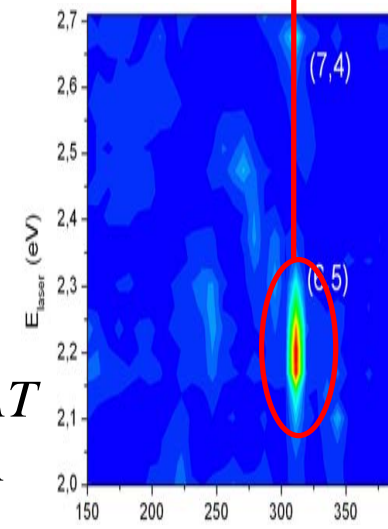
HiPco+ SDS
Strano



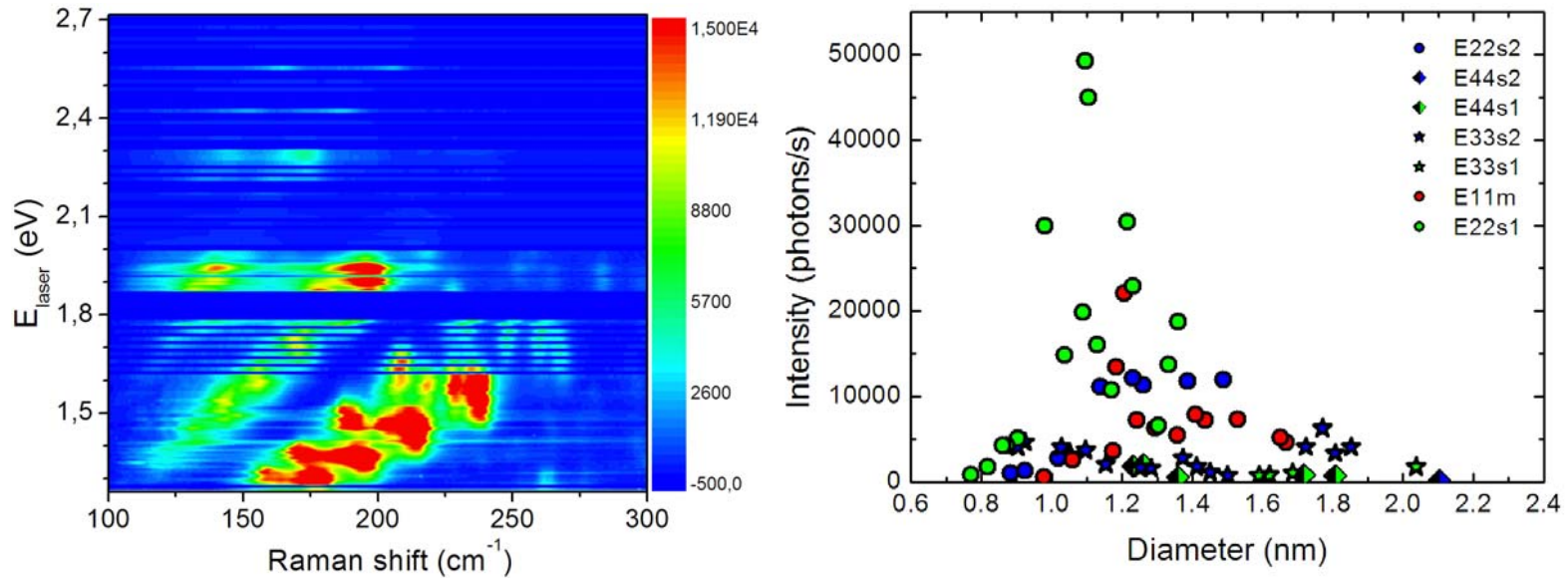
CoMoCAT
+ *SDS*
Resasco



CoMoCAT
+ *DNA*



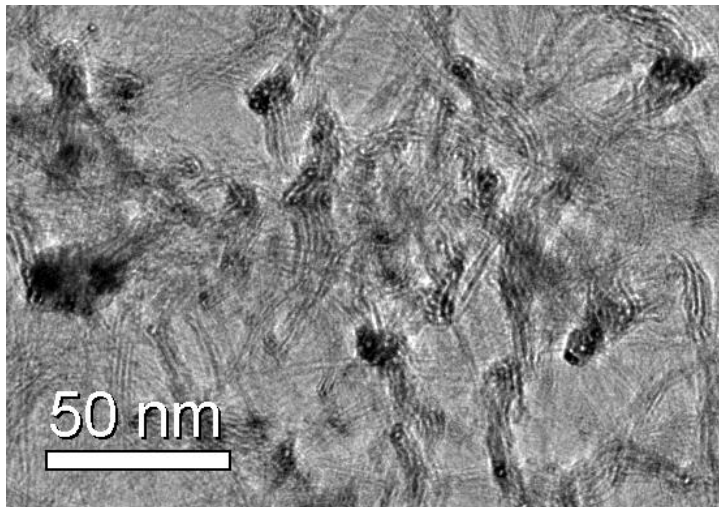
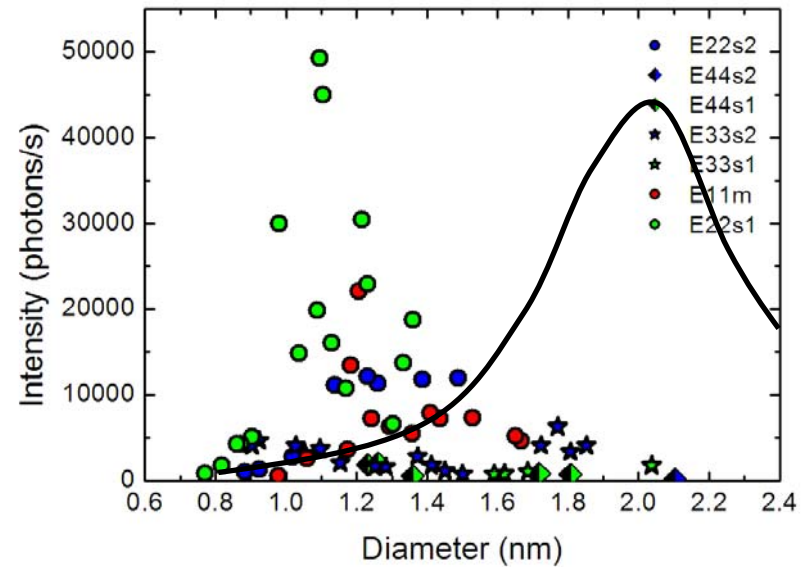
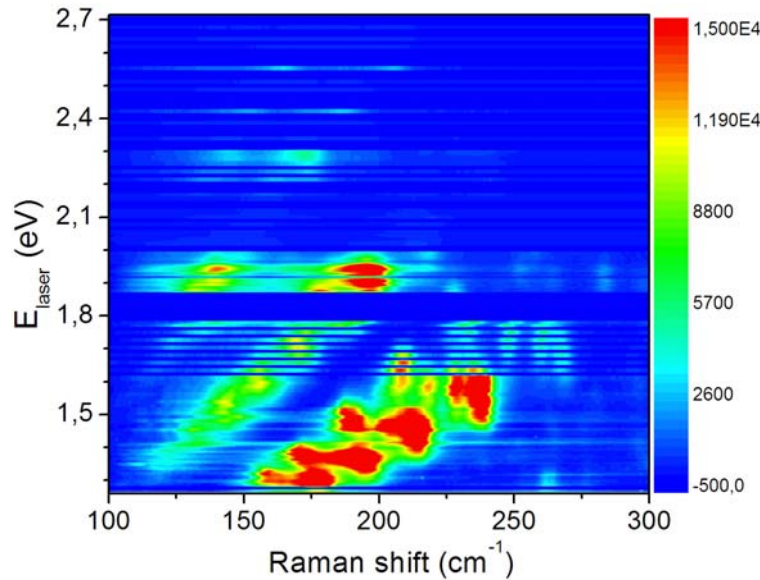
(n,m) dependence for SWNTs RRS cross section



**Raman (or generally optics) strongly pushes
your d_t distribution to lower diameters?**

d_t distribution: RRS vs. TEM

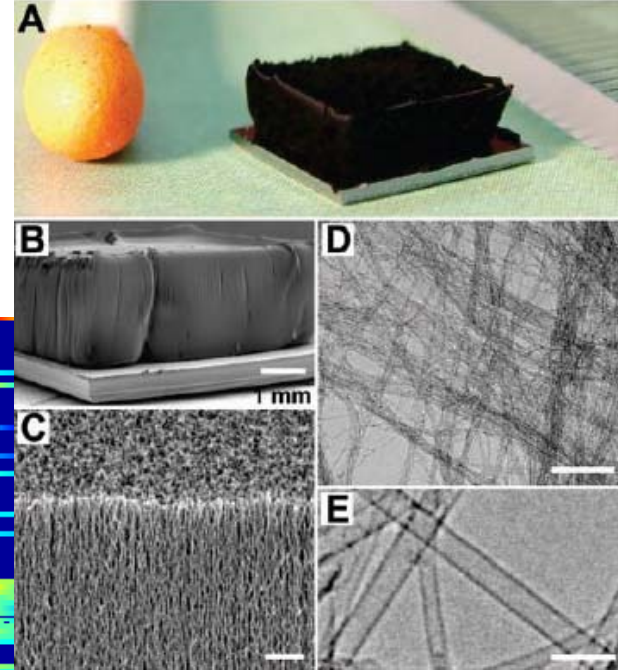
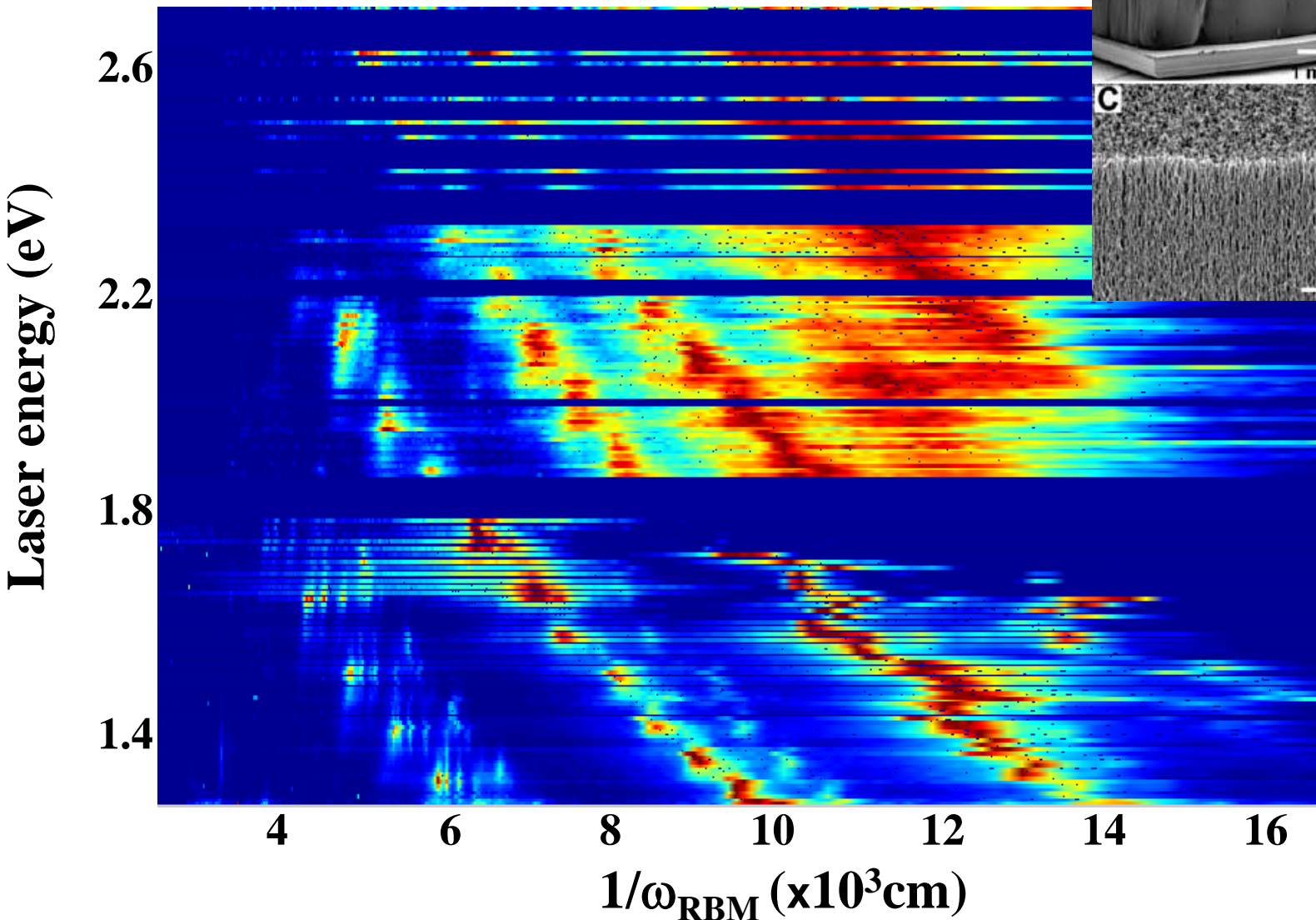
Intensity analysis is a very serious issue that requires more work



d_t distribution based on TEM:
0.8 to 3.0 nm
average 2.0 nm,
standard deviation 0.4 nm

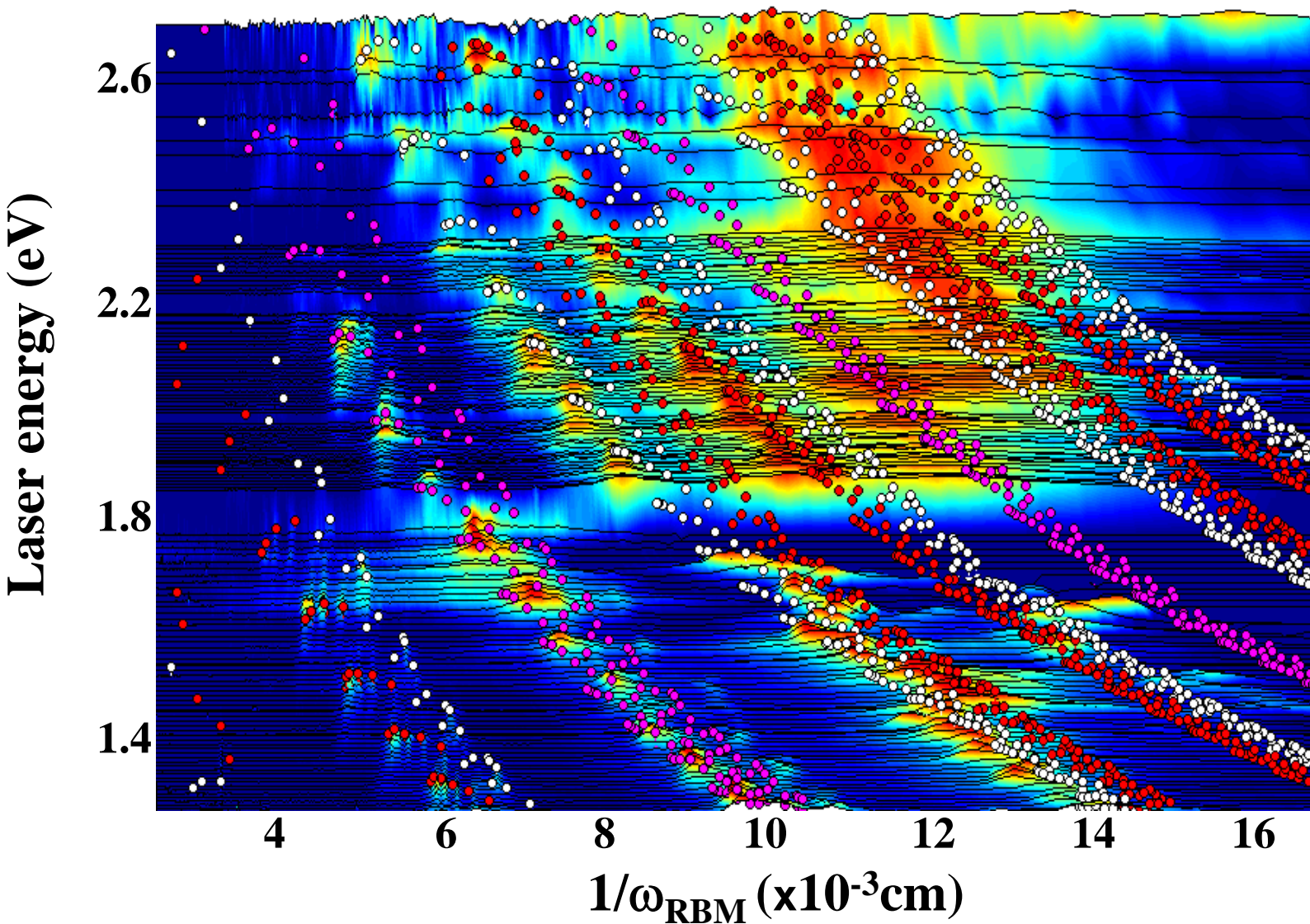
Y. Murakami et al.
Carbon **43**, 2664 (2005)

Isolated SWNTs with d_t up to 4nm
and E_{ii} up to E_{66}^S and E_{22}^M



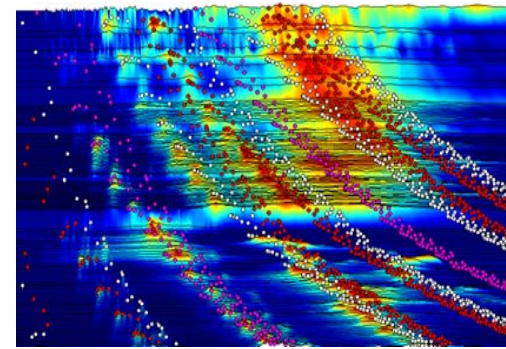
Sample:
SWNTs carpet
CVD
K. Hata et al.
Science 306,
1362 (2004)

Isolated SWNTs with d_t up to 4nm and E_{ij} up to E_{66}^S and E_{22}^M

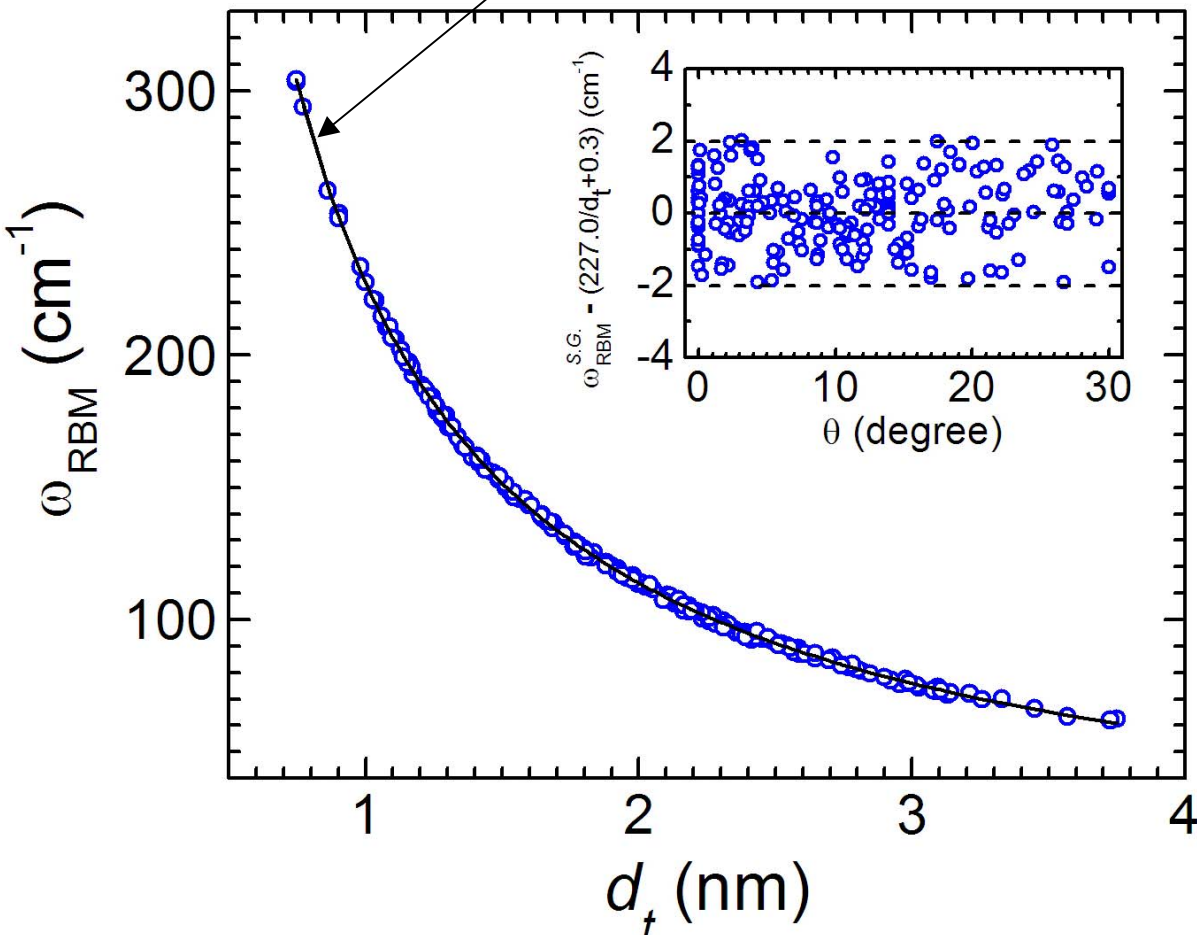


ω_{RBM} vs. d_t

$$F/a = \lambda \delta b/b \rightarrow \omega_{\text{RBM}} = \frac{1}{\pi d_t} (\lambda/\sigma)^{1/2}$$



$$\omega_{\text{RBM}} = A/d_t + B$$



$$A = 227.0 \pm 0.3 \text{ (cm}^{-1}\text{nm)}$$

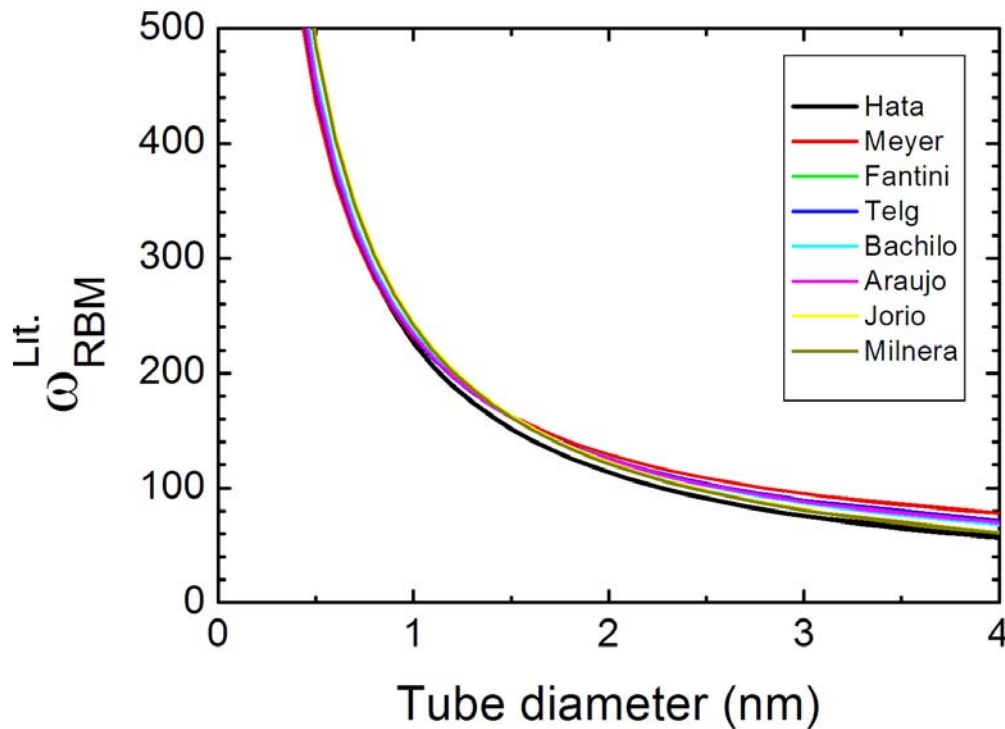
exactly the value
expected from the
elasticity theory and the
speed of sound in
graphite

$$B = 0.3 \pm 0.3 \text{ cm}^{-1}$$

$\omega_{\text{RBM}} \rightarrow \infty$
as $d_t \rightarrow 0$

Comparing the results from the literature

$$\omega_{\text{RBM}} = A/d_t + B$$



$$d_t = a_{\text{C-C}} \sqrt{3(n^2 + mn + m^2)} / \pi$$

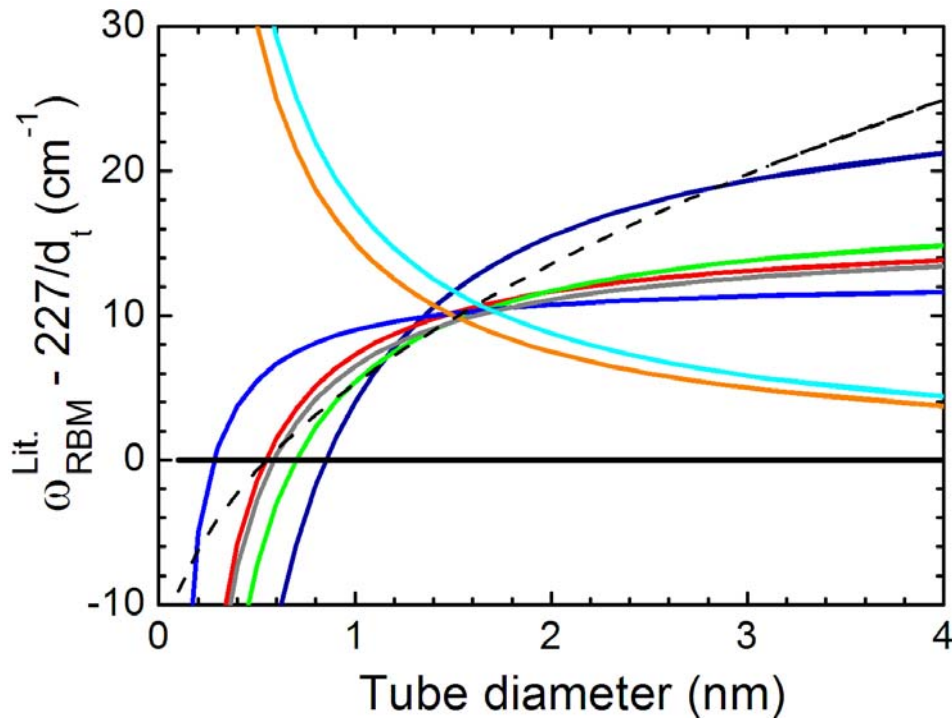
$$a_{\text{C-C}} = 0.142 \text{ nm}$$

A	B	# of SWNTs
248(244.5)	0	17 (<i>Jorio</i>)*
242	0	Bundle (<i>Milnera</i>)*
223.5	12.5	10 (<i>Bachilo</i>)
214.4	18.7	48 (<i>Telg</i>)
218.3	16	46 (<i>Fantini</i>)
204	27	11 (<i>Meyer</i>)
218	16	94 (<i>Araujo</i>)
227	0	197 (<i>Araujo</i>)

*Obtained based on simple (first-neighbors) tight binding calculations

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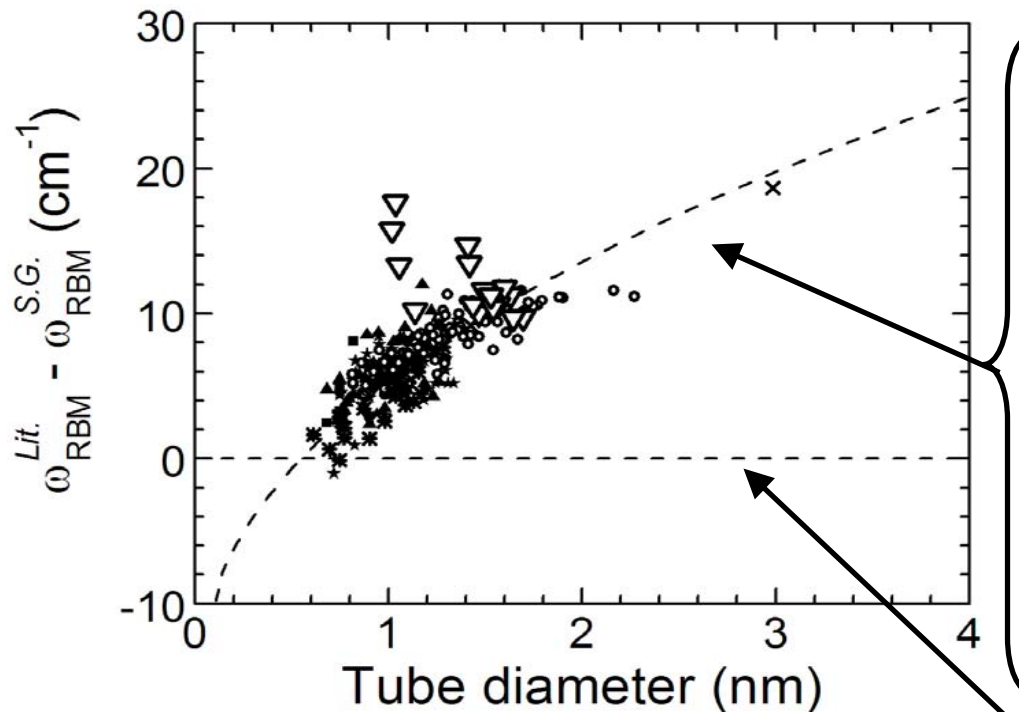
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Comparing the results from the literature

$$\omega_{\text{RBM}} = 227/d_t + (?) \rightarrow \Delta\omega_{\text{RBM}} = (-16.7) + 22d_t^{0.46}$$



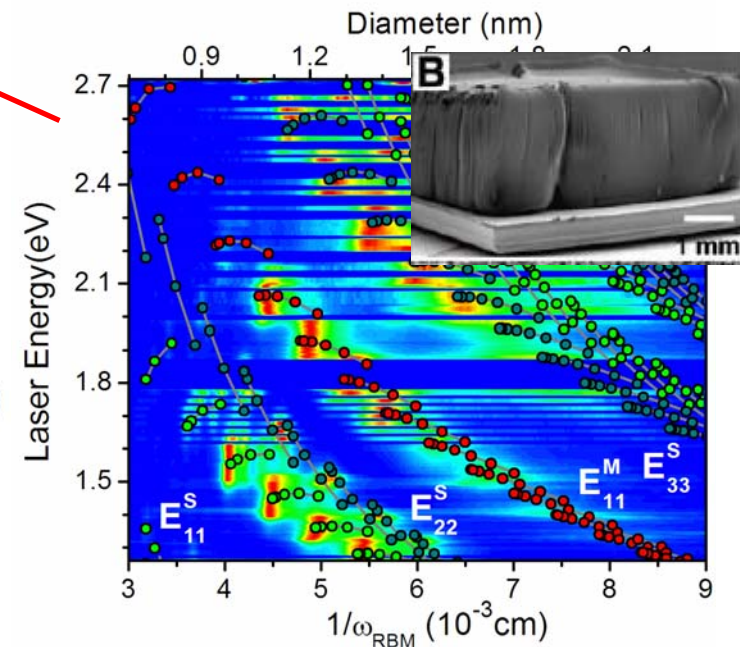
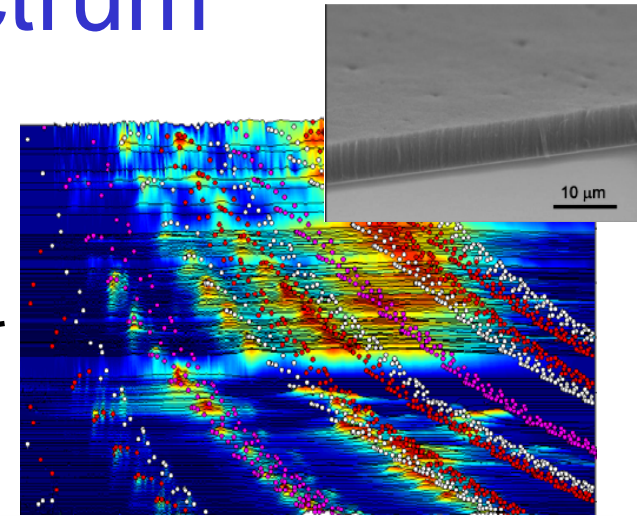
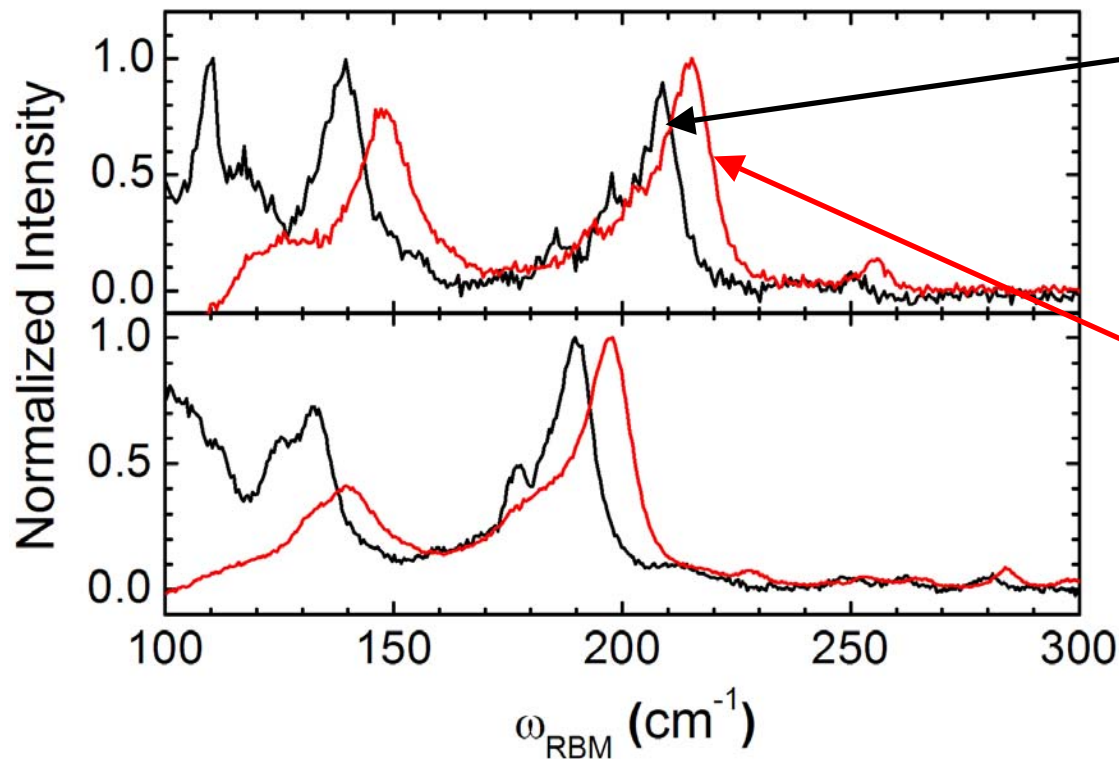
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$$d_t = a_{\text{C-C}} \sqrt{3(n^2 + mn + m^2)} / \pi$$

$$a_{\text{C-C}} = 0.142 \text{ nm}$$

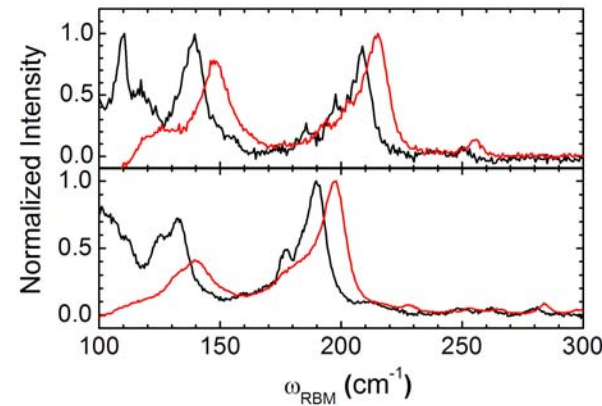
*Obtained based on simple (first-neighbors) tight binding calculations

The effect is measurable by looking at one single spectrum

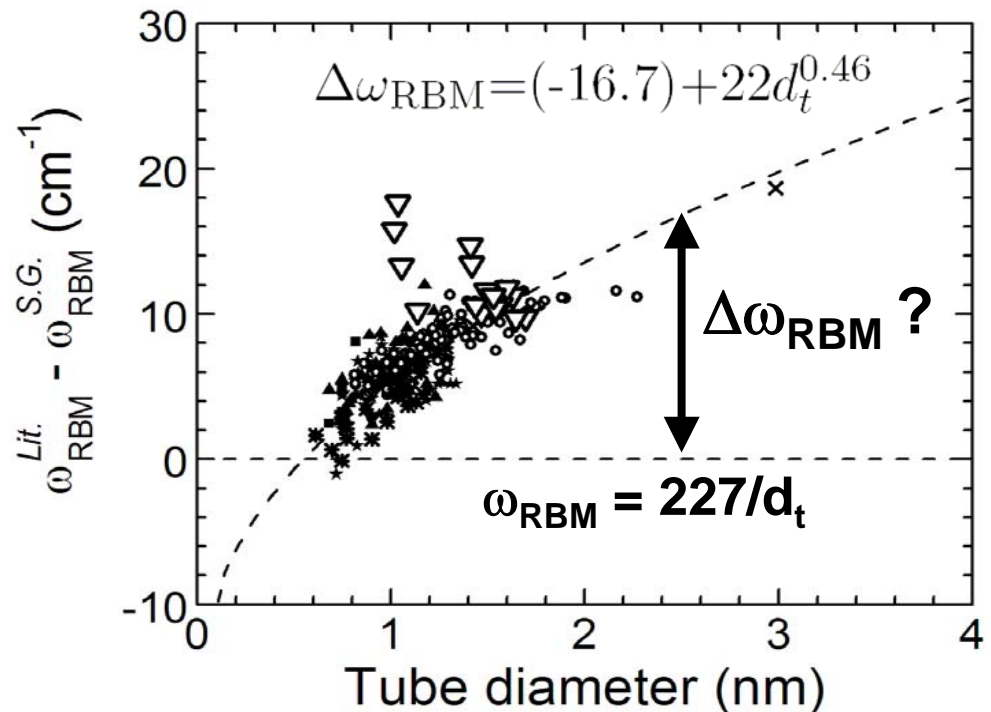


What is the physical origin?

$$\omega_{\text{RBM}} = \frac{1}{\pi d_t} (\lambda/\sigma)^{1/2}$$

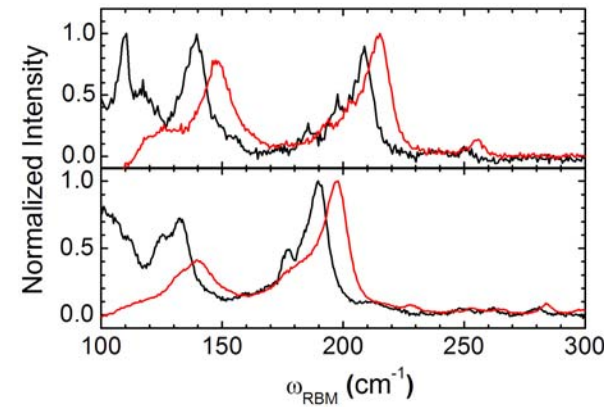


$$\delta\omega/\omega = -\delta d_t/d_t + (1/2)\delta\lambda/\lambda - (1/2)\delta\sigma/\sigma$$



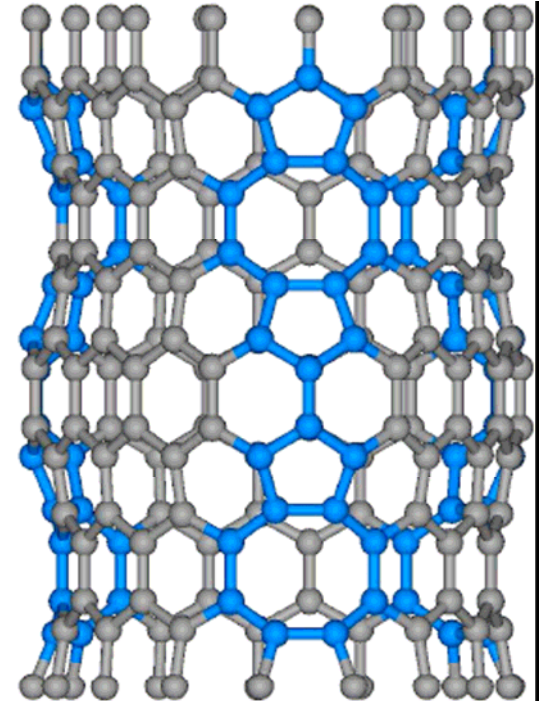
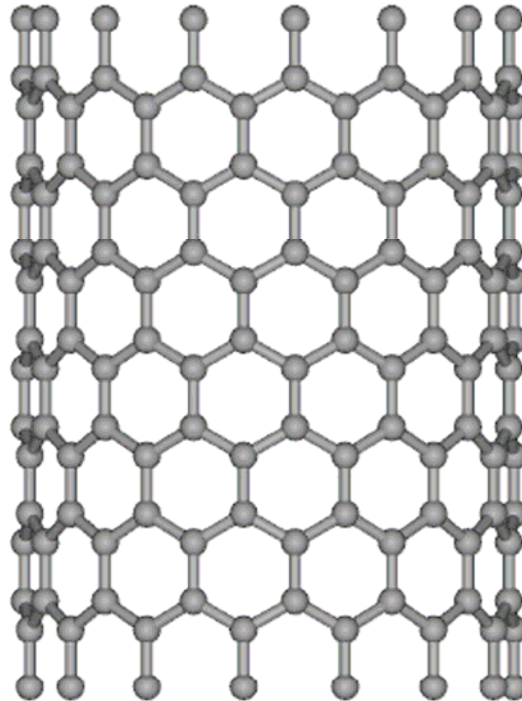
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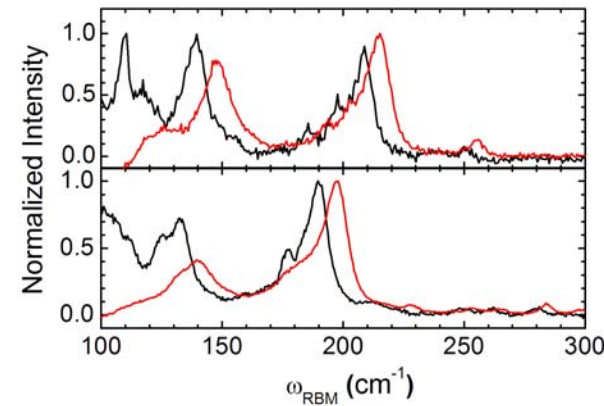
$$\delta\omega/\omega = -\delta d_t/d_t + (1/2)\delta\lambda/\lambda - (1/2)\delta\sigma/\sigma$$

**Calculations show
that divacancies
cause an ω_{RBM}
upshift of about 5%,
as observed
experimentally**



What is the physical origin?

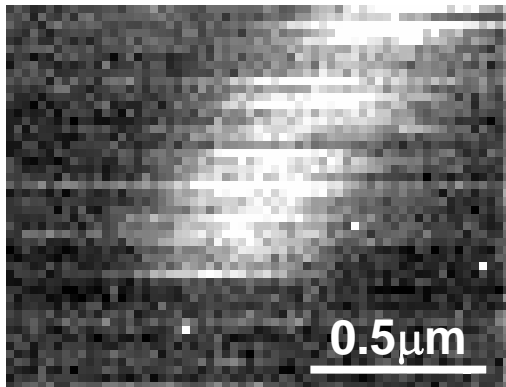
$$\omega_{\text{RBM}} = \frac{1}{\pi d_t} (\lambda/\sigma)^{1/2}$$



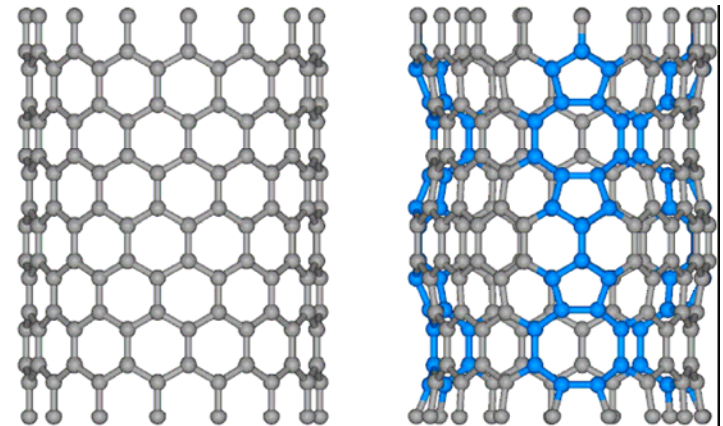
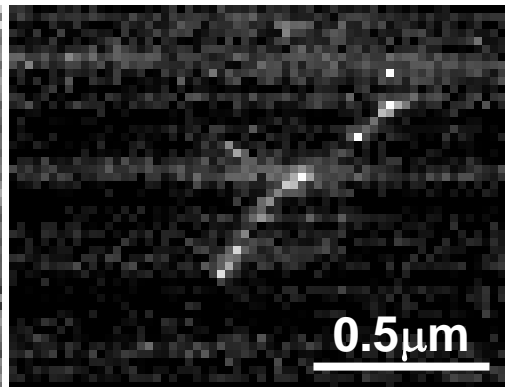
$$\delta\omega/\omega = -\delta d_t/d_t + (1/2)\delta\lambda/\lambda - (1/2)\delta\sigma/\sigma$$

NSOM shows localized optical emission

Far-field PL

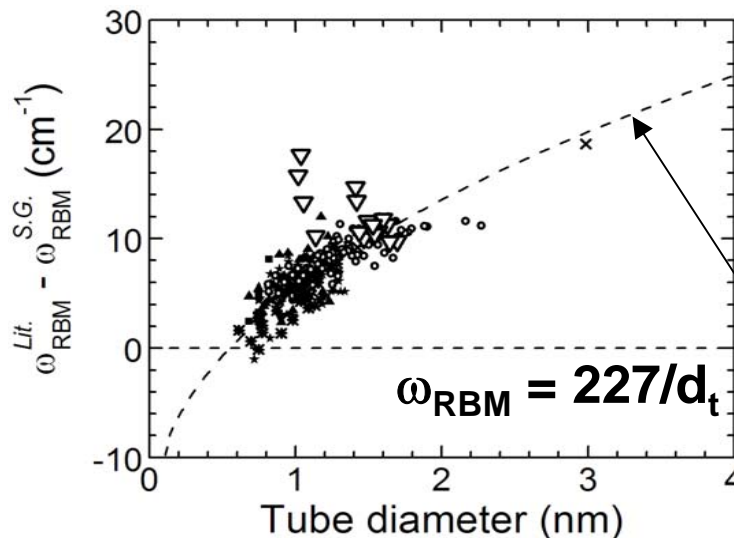
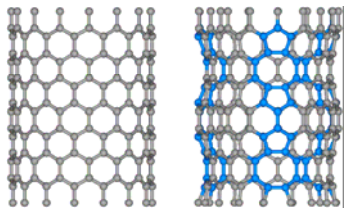


Near-field PL



Summary and conclusions

- All RBM data from the literature have been fitted with $\omega_{\text{RBM}} = A/d_t + B$, with arbitrary A and B considerably different from zero
- Thinking of “nano-bulk consistency”, this result is unacceptable
- There is a sample where $\omega_{\text{RBM}} = 227/d_t$, obeying “nano-bulk consistency” perfectly. Can it be considered a reference standard?



A exactly matches the value expected from the elasticity theory and the speed of sound in graphite

$$B = 0$$

$$\omega_{\text{RBM}} \rightarrow \infty \text{ as } d_t \rightarrow 0$$

$$\Delta\omega_{\text{RBM}} = (-16.7) + 22d_t^{0.46} ?$$

- What is the (n,m) dependence for the Raman cross section?

Acknowledgements

P. T. Araujo, P. B. C. Pesce, I. O. Maciel, M. A. Pimenta, H. Chacham

M. S. Dresselhaus group

R. Saito group

A. Hartschuh, S. K. Doorn and L. Novotny groups

D. Resasco, M. Strano, S. Maruyama and K. Hata groups.

Support from NIST

Thank you for your attention!

Please join us at MSIN08 (*Montpelier*)!!!